LIQUID DEVELOPER FOR ELECTROPHOTOG RAPHY CONTAINING THE REACTION PRODUCT OF A DYESTUFF AND A FATTY ACID

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No Drawing. Filed Dec. 16, 1969, Ser. No. 885,626

Claims priority, application Japan, Dec. 18, 1968, 45/92,573

Int. Cl. G03g 9/04

U.S. Cl. 252—62.1

5 Claims

ABSTRACT OF THE DISCLOSURE

A liquid developer for electrophotography which comprises a dispersion of a salt-forming reaction product between at least one dyestuff or dyestuff base containing amino groups and at least one fatty acid of not less than 8 carbon atoms, in a high electric resistance liquid as carrier, said fatty acid being soluble in said carrier liquid; characterized in that a salt formed from said fatty acid and said dyestuff or dyestuff base is insoluble in said high electric resistance liquid, and that said fatty acid is present in an amount of at least 4 moles per mole of said dyestuff or dyestuff base, the amount of said fatty acid being sufficient to disperse said salt in the fine divided state stably in the carrier liquid but being not so excessive as to cause any bleeding of an image to be formed.

This invention relates to a liquid developer for electrophotography which comprises a dispersion of a salt-forming reaction product between a dyestuff or dyestuff base containing amino groups and a fatty acid of not less than 8 carbon atoms, in a high electric resistance liquid as carrier. More particularly, the invention relates to such liquid developer for electrophotography, in which the mol ratios of the dyestuff or dyestuff base to the fatty acid within a specific range are employed to improve the dispersibility and stability of the liquid developer, and to form distinct images of good fixing property.

Methods of developing electrostatic latent images in electrophotography can be classified into two large cate-
gories of dry developing such as cascade development method, magnetic brush development method and powder cloud development method using dry coloring agent powder, and liquid developing using developers comprising a dispersion of coloring material such as pigments in a high electric resistance liquid.

This invention belongs to the category of the latter liquid developing. In the early liquid developing methods such as those disclosed in British Pat. No. 755,486 or French Pat. No. 1,112,180, as the means of developing electrostatic latent images into visible images, powder which will be electrically drawn to the images, such as carbon black, is dispersed in a high electric resistance liquid which is an organic liquid, such as various hydrocarbons, carbon tetrachloride, and ordinary insulating oil, etc.

Also Journal of Scientific Instruments, vol. 32, p. 74 (1955), and Ibid. vol. 33, p. 194 (1956) discloses dispersions of pigments such as talce, magnesium, carbon black, Monolite Red RS, Monolite Yellow GNS, Rhthalocyanine Blue (Waxoline Nigrosine), zinc oxide, Hansa Yellow and cadmium sulfide, in a high electric resistance liquid such as turpentine, oil, gasoline, kerosene, benzene, and carbon tetrachloride, to which further linseed oil or synthetic resin is added for controlling charge on the coloring powder and fixing visible images.

Japanese Patent No. 273,198 (Japanese Official Patent Gazette, Publication No. 13,424/60) teaches the developer formed by dispersing a pigment in a high electric resistance liquid, said pigment being coated with such a substance as alkyl resin, linseed oil, synthetic rubber, polyurethane, wax rubber, or the like which are referred to as a control agent, in order to make the pigment electrically selective to the charge of latent images.

After the above Japanese patent, many studies and experiments were reported, aiming at effective control of charge polarity of dispersed particles of coloring material, improvement of stability of the dispersion and fixing of finished images, and additions of various synthetic and natural resins, synthetic resin monomers, primary condensates thereof, surface active agents and the like as the substance to coat the particles of coloring material such as pigment or to be dissolved in the electrically resistant liquid acting as the carrier liquid have been proposed.

The important problems in liquid developers in general reside, first in the uniformity and dispersion stability of the charged particles which are dispersed in the carrier liquid, and second, in the distinction and fast fixing of the images formed by developing.

However, conventional liquid developers herefore known are subject to serious defects with respect to storage stability and duration of activity. That is, excellent dispersing condition is observed in the developers immediately after dispersing the coloring material, and distinct images can be developed therewith, but the balance between the carrier liquid and coloring material as well as aforementioned additives is lost with time passage under continuous usage or storage, resulting in aggregation of particulate coloring material, deterioration in electrical properties such as uniformity in charge polarity, precipitation of particles, and increasing obscuring in the finished images developed with the liquid. Thus the developers become unsuitable for practical use.

Generally speaking, additives which are excellent as dispersing agents of coloring material gradually deteriorate the electrical insulating property of the carrier liquid, and cause the charge of particulate coloring material to disappear gradually. Also the additives to reinforce fixing property often precipitate as the result of oxidation, polymerization, gelation, etc. Furthermore, the control agent to coat the pigment particles not only gradually loses its controlling activity as dissolved in the carrier liquid or separated from the pigment particles, but also induces aggregation and precipitation of pigment particles, making the formed images very obscure.

Thus, heretofore known liquid developers may possess excellent dispersibility and distinct image-forming ability immediately after their preparation, but are subject to a fatal defect in practical use that they lack storage stability and they lose reproducibility of images with the lapse of time.

We have now discovered that, quite independently of the conventional techniques of adding such modifiers as a control agent, dispersing agent, fixing agent, etc. to the
carrier liquid together with coloring material, a dispersion of a salt-forming reaction product between a dyestuff or dyestuff base containing amino groups and a fatty acid of not less than 8 carbon atoms which is soluble in a liquid to be used as high electric resistance liquid, in said liquid or in a carrier in which the mol ratios of the dye- stuff or dyestuff base and the fatty acid is within a specific range, is an effective liquid developer for electrophotography exhibiting excellent storage stability, distinctness and fixing property of images, and reproducibility of images over prolonged period.

Accordingly, one object of the present invention is to provide a liquid developer for electrophotography which exhibits excellent storage stability during storage and reproducibility of image formation over prolonged period and which can form distinct images with high fixing property.

Another object of the invention is to provide a liquid developer for electrophotography in which the coloring material dispersed in the carrier liquid itself possesses excellent fixing ability and uniform charging characteristic.

According to this invention, there is provided a liquid developer for electrophotography which comprises a dispersion of a salt-forming reaction product between at least one dyestuff or dyestuff base containing amino groups and at least one fatty acid of not less than 8 carbon atoms, in a high electric resistance liquid as the carrier, said fatty acid being soluble in said carrier liquid, characterized in that a salt formed from dyestuff or dyestuff base and said fatty acid is soluble in said high electric resistance liquid and that said fatty acid is present in an amount of at least 4 mols per mol of said dyestuff or dyestuff base, the amount of said fatty acid being sufficient to disperse said salt in the finely divided state stably in the carrier liquid but not being so excessive as to cause any bleeding of an image to be formed.

In the present specification the term “salt” is intended to mean a kind of a fatty acid salt formed by combining of the dyestuff or dyestuff base containing amino groups which is a base, with the fatty acid which provides acid radicals. Also the term “salt-forming reaction product” means a reaction product mixture formed upon reacting the dyestuff or dyestuff base containing amino groups with the fatty acid in order to make the above-specified “salt.”

Any fatty acid can be used in the present invention as long as it is soluble in the high electric resistance liquid employed, and contains at least 8 carbon atoms, although fatty acid of 10-30 carbon atoms are preferred for obtaining good dispersion stability of the salt of said acid with the dyestuff or dyestuff base in the carrier liquid. For example, saturated fatty acids such as capric, lauric, myristic, palmitic, stearic, and arachidic acids; and unsaturated fatty acids such as oleic, zearomeric, linoleic, linolenic, elaeostearic, morocotic, clupanodonic, nisinic, and ricinoleic acids, can be used. Also hydrogenated oils of the foregoing acids may be used. It is of course permissible to use mixtures of those fatty acids. For example, fatty acid mixtures obtained through hydrolysis of natural fat and oil such as animal and vegetable oils may be used.

In the present invention, it is particularly important that the fatty acid employed is soluble in the high electric resistance liquid. When a fatty acid which is substantially insoluble in the high electric resistance liquid is used, liquid developers of excellent dispersion stability cannot be formed. For example, oleic acid is soluble in almost all liquid hydrocarbons, including even isoparaffin-type hydrocarbons having low dissolving power. However, stearic acid is also soluble in isoparaffin-type hydrocarbons in summer, but the solubility is considerably reduced in winter, while it will be soluble to an appreciable degree in aromatic hydrocarbons or mixtures of aromatic hydrocarbons with aliphatic hydrocarbons. Fatty acids which exhibit broad adaptability to various liquid hydrocarbons and seasons and consequently are preferred for the pur-
pose of this invention are unsaturated fatty acids, particularly oleic acid.

According to the invention, the salt-forming reaction product of such fatty acid with a dyestuff or dyestuff base containing amino groups is dispersed in a high electric resistance liquid. In that procedure, the salt of the fatty acid with the dyestuff or dyestuff base must be insoluble in the high electric resistance liquid. If the salt is soluble in said liquid, distinct images cannot be formed.

It is extremely important for the invention that in said dispersing step, the quantity of the fatty acid should be at least 4 mols per mol of the dyestuff or dyestuff base, being sufficient to finely divide and disperse said salt in the liquid but not so much as to cause the bleeding of an image to be formed, for achieving the intended improvements in the developers' storage stability, distinctness and fixing property of images, and in the reproducibility of image formation over prolonged period.

The reason why the subject liquid developer exhibits excellent storage stability and image-reproducibility over prolonged periods is not yet thoroughly understood, but our presumed reason is as follows.

When the salt-forming reaction product of the dyestuff or dyestuff base containing amino groups with the fatty acid is dispersed in the carrier liquid, dissociation equilibrium as expressed by the formula below is reached.

\[
(R-CO_2-\text{NH}+\text{R'NR}_2)\overset{\text{D}}{\rightleftharpoons} D-(\text{R'NR}_2)+R-COOH \quad (1)
\]

in which

\(R\) denotes a long chain alkyl or alkene group of at least 7 carbon atoms, preferably 9-29 carbon atoms,

\(D\) is the dyestuff residue,

each of \(R'\) and \(R''\) is hydrogen or a dyestuff residue, and

\(n\) is an integer of not less than 1.

Thus, if the salt of the dyestuff or dyestuff base with the fatty acid is simply dispersed in the carrier liquid, the salt is dissociated into the fatty acid and the dyestuff or dyestuff base, and because the dyestuff or dyestuff base generally lacks dispersibility in the carrier liquid, uniform charging ability, and fixing property, the storage stability and image-reproducibility over prolonged period of the liquid developer tend to be deteriorated.

On the other hand, in the dispersing step of the salt-forming reaction product between the dyestuff or dyestuff base containing amino groups and the fatty acid in a high electric resistance liquid, if the fatty acid is caused to be present in an amount of at least 4 mols per mol of the dyestuff or dyestuff base and furthermore excessive within a specific range depending on the type of dyestuff or dyestuff base and the type of fatty acid, the mobility of equilibrium to the right, i.e., the tendency of freeing the dyestuff or dyestuff base, is inhibited, and the salt dispersed in the liquid is stabilized.

Furthermore, the salt of a dyestuff or dyestuff base with a fatty acid normally very easily dissolves and disperses in excessive fatty acid, to form as a whole a homogeneous solution or solid solution. The salt of the dyestuff or dyestuff base with a fatty acid is not only maintained in the solution or solid solution with high stability, but when the solution or solid solution is dispersed in a high electric resistance liquid which is a non-solvent, with optional intervening heating, it is made possible to disperse the image-forming material as fine particles, with high stability than any that can be obtained with mechanical stirring or shearing. In that case, if the excessive fatty acid is dissolved in the high electric resistance liquid, it will probably contribute to the stability of the salt of the dyestuff or dyestuff base and the fatty acid, as illustrated by the foregoing equation of equilibrium.

Thus, since in the liquid developer of the invention the salt-forming reaction product between a dyestuff or dyestuff base and a fatty acid with which the image-forming material is self-stabilized by the action of chemical equilibrium of the
dyestuff or dyestuff base and the fatty acid and, furthermore, since the salt-forming reaction product is homogeneous, the liquid developer is completely free of the defects inherent in the conventional liquid developers in which the pigment particles are simply mechanically coated with a control agent, such as poor storage stability and image-reproducibility over prolonged period.

According to the invention, it is necessary to make the fatty acid present in an amount of at least 4 mols per mol of the dyestuff or dyestuff base which is not yet converted to the salt, the amount furthermore being sufficient to disperse the salt or salt-forming reaction product between the fatty acid and the dyestuff or dyestuff base in the finely divided state stably in a high electric resistance liquid. The lower limit in the amount of the fatty acid meeting the above requirement differs depending on the type of the dyestuff or dyestuff base, and the type of the fatty acid, but generally is within the range of 4-1,000 mols per mol of the dyestuff or dyestuff base. The suitable amount for individual case can be easily determined by simple experiments.

On the other hand, if the excessive amount of the fatty acid to the dyestuff or dyestuff base is too large, there occurs a tendency that the image formed by developing the electrostatic latent images become fluid, which is normally referred to as “bleeding images.”

Therefore, the upper limit in the amount of the fatty acid is determined as much as which will not yield the formed images fluid. Such an amount is rather variable depending on such factors as the type of the dyestuff or dyestuff base, type of the fatty acid, and fatty acid concentration in the dispersion liquid, but can be easily determined for each individual case by simple experiments, within the aforesaid range of 4-1,000 mols per mol of the dyestuff or dyestuff base.

More specifically, in case the fatty acid is oleic acid it is preferable to make it present in an amount of 10 to 400 mols per mol of the dyestuff or dyestuff base. In the case of stearic acid, it is preferable to make it present in an amount of 4 to 40 mols per mol of the dyestuff or dyestuff base. When linoleic acid is used as the fatty acid, a preferable amount is 10 to 200 mols per mol of the dyestuff or dyestuff base. In the case of capric acid, a preferable amount is within a range of 40 to 200 mols per mol of the dyestuff or dyestuff base. In the case the fatty acid is Iuric acid, it is preferable to make it present in an amount of 10 to 200 mols per mol of the dyestuff or dyestuff base. In the case of palmitic acid a preferable amount ranges from 10 to 100 mols per mol of the dyestuff or dyestuff base.

The type of the dyestuff or dyestuff base to be employed for producing the salt-forming reaction product in accordance with the invention is not critical, as long as it contains amino groups which can form a salt with a fatty acid, and the salt or salt-forming reaction product is insoluble in the high electric resistance liquid. Examples of such dyestuff or dyestuff base include those possessing amino groups capable of forming a salt with a fatty acid, selected from basic azo dyes, basic diphenylmethane dyes, basic triphenylmethane dyes, acredine dyes, pyrmine dyes, Rhodamine dyes, quinoline dyes, azo-type disperse dyes, and anthraquinone dyes.

Such dyestuff or dyestuff base can be used singly or in combination. Visible image of desired color tone can be obtained by combined use of more than one dyestuffs or dyestuff bases of different color tones, or further varying the quantitative ratios of such plural dyestuffs or dyestuff bases. Because the image-forming material of this invention is extremely homogeneous as particles themselves as well as in interrelations of the particles, the developer never causes uneven coloring due to non-uniform electrodeposition rates and charges among the particles, nor change in color tone occurring with the developer deterioration with time passage, unlike the conventional mere mixtures of dyestuffs or pigment particles, or other particulate coloring material.

Specific examples of useful dyestuffs and dyestuff bases include the following:

(1) BASIC AZO DYES
- Chrysoidine Base [C.I. solvent orange 3 (112708)]
- Bismarck Brown G Base [C.I. basic brown 1 (21000)]

(2) BASIC DIPHENYL METHANE DYES
- Auramine [C.I. basic yellow 2 (41000)]
- Auramine Base [C.I. solvent yellow 34 (41001 B)]

(3) BASIC TRIPHENYL METHANE DYES
- Malachite Green [C.I. basic green 4 (42000)]
- Malachite Green Base [C.I. solvent green 1 (42000 B)]
- Magento [C.I. basic violet 14 (42510)]
- Magenta Base [C.I. solvent red (42510 B)]
- Methyl Violet [C.I. basic violet 1 (42535)]
- Crystal Violet [C.I. basic violet 3 (42555)]
- Crystal Violet Base [C.I. solvent violet 9 (42555 B)]
- Victoria Blue [C.I. basic blue 26 (44045)]
- Victoria Blue Base [C.I. solvent blue 4 (44045 B)]
- Soluble Blue [C.I. solvent blue 23 (47601)]
- Patent Blue AF: intermediate product before sulphonation of [C.I. acid blue 7 (42080)]

(4) ACRIDINE DYES
- Acridine [C.I. basic orange 14 (46005)]
- Phenone AL [C.I. basic dye 46005]

(5) PYRONINES
- Pyronine G [C.I. basic dye 45005]

(6) RHODAMINES
- Rhodamine 3B [C.I. basic violet 10 (45170)]
- Rhodamine 3B Base [C.I. solvent red 49 (45170 B)]

(7) QUINONEIMINE DYES
(Azine type)
- Safranine T [C.I. basic red 2 (50340)]
- Indoline [C.I. solvent blue 7 (50400)]
- Nigrosine [C.I. solvent black 5 (50415)]
- Nigrosine Base [C.I. solvent black 7 (50415 B)]

(Oxazine type)
- Meldola’s Blue [C.I. basic blue 6 (51175)]
- Meldola’s Blue [C.I. basic blue 6 (51175)]

(Thiazine type)
- Methylene Blue [C.I. basic blue 9 (52015)]
- Methylene Blue Base [C.I. solvent blue 8 (52015 B)]

(8) AZO TYPE DISPERSE DYES
- Celloint Fast Orange GR [C.I. disperse orange 3 (11005)]

(9) ANTHRAQUINONE TYPE DISPERSE DYES
- Sudan Violet R [C.I. disperse violet (61100)]
- Celloint Blue Extra [C.I. disperse blue 1 (64500)]
- Disperse Fast Brilliant Blue B [C.I. disperse blue 3 (61051)]

In the present invention, the high electric resistance liquid used as the dispersion medium can be any organic liquid which dissolves the fatty acid specified in the foregoing, but does not dissolve the salt or salt-forming reaction product between the fatty acid and the dyestuff or dyestuff base, and which has an electric resistance of at least 10⁶ Ω-cm, preferably not less than 10⁸ Ω-cm. Thus, in accordance with the invention, straight or branched chain aliphatic hydrocarbons such as n-hexane, n-octane
and isoparaffin; alicyclic hydrocarbons such as cyclohexane terpenes; aromatic hydrocarbons such as benzene and toluene; halogenated hydrocarbons such as trichloroethylene, methylene chloride and fluorinated hydrocarbon; and silicones such as dialkyl and diphenyl silicones can be used. Of course it is permissible to use mixtures of those solvents, for example, mixed hydrocarbons of naphtha, kerosene and the like. In the present invention, use of liquid hydrocarbons, particularly isoparaffin type hydrocarbons is preferred.

The liquid developer of the invention can be prepared by the following procedures. A fatty acid or fatty acid mixture and a dyestuff or dyestuff base are heated in the optional presence of a suitable solvent, to form a salt of the fatty acid with the dyestuff or dyestuff base. In that reaction, the amount of the fatty acid to the dyestuff or dyestuff base should be within the afore-specified range. For example, when the combination of Nigrosine Base and oleic acid is used with isoparaffin, a suitable amount of oleic acid is 4-800 mols per mol of the base, preferably 10-200 mols. The salt-forming reaction of the fatty acid with the dyestuff or dyestuff base is performable at room temperature, but it is preferred to employ elevated temperatures of 50-150°C. in order to sufficiently complete the reaction. If side reaction or reactions other than the salt formation take place to a slight degree, such is not appreciably detrimental to the results of this invention. The completion of the salt-forming reaction can be normally confirmed by color change in the reaction mixture. The salt-forming reaction product in this stage can be normally obtained in the state ranging from homogeneous solution to highly viscous, semi-solid, or fully solid solution.

The salt-forming reaction product in solution to solid solution form is added to the high electric resistance liquid described in the foregoing, to be finely divided and dispersed in the latter, if necessary, with the aid of ultrasonic waves or high shearing force agitation. The salt-forming reaction product may be used at the concentrations useful for developing electrostatic latent images, that is, the concentrations of 0.005 to 0.3 wt. percent based on the carrier liquid, or may be used at concentrations as high as 30 wt. percent or even higher, so that the product may be diluted with the carrier liquid immediately before actual use.

The liquid developers of the invention may also be prepared by the steps of forming the salt using the fatty acid in an amount less than the desired, for example, in stoichiometric amount required for the salt formantion, adding to the resulting salt forming reaction product the remaining amount of fatty acid to form a homogeneous solution, and dispersing the solution in the carrier liquid.

Or, a hydrochloride of the dyestuff or dyestuff base may be reacted with an alkali metal salt of the fatty acid, i.e., soap, at stoichiometric amounts, and the resulting fatty acid salt may be refined and dissolved in the fatty acid, followed by dispersing of the solution in a carrier liquid.

Thus, in the liquid developer for electrophotography of the invention, the salt or salt-forming reaction product between the fatty acid and the dyestuff or dyestuff base which is the image-forming material is stably maintained in the form of fine particles in the carrier liquid by the action of chemical equilibrium caused by excess fatty acid, and the dispersion stability is not impaired by storage. Furthermore, the image-forming material in the liquid developer of the invention is itself homogeneous, and never alters or causes charge variation during storage. Still in addition, the image-forming material in the liquid developer of the invention, i.e., the salt or salt-forming reaction product between the fatty acid and the dyestuff or dyestuff base, itself possesses fixing onto sensitive layer.

Accordingly, the invention successfully provides a liquid developer for electrophotography exhibiting excellent storage stability, distinctness and fixing property of images, and image-reproducibility over prolonged periods.

The invention will be hereinafter explained with reference to the working examples.

**EXAMPLE 1**

To 20 g. of oleic acid heated to 50°-60°C., 1 g. of Nigrosine Base was gradually added under stirring. Thereafter the stirring was continued while the mixture was further heated to approximately 95°C., and maintained at said temperature for an hour. The system was subsequently allowed to stand until the temperature was cooled off to 20°-30°C. Two (2) grams of thus-formed homogeneous, viscous salt-forming reaction product was added to 1 liter of Isopar H (product of Esso Standard Petroleum Co.) which is an isoparaffin type solvent, to form a dispersion of extremely fine particles. This liquid developer exhibited excellent suspension quality and hardly formed precipitates. In order to examine the polarity of the particles in the developer, two metal plate electrodes were inserted into the liquid developer spaced by 1 cm., and direct current of 1,000 volts was applied for 60 seconds. Thereafter the electrodes were withdrawn from the developer, and the state of adhesion of the particles on the electrode surface was examined. As the result it was confirmed that the particles possessed 100% positive charge. The particles in the developer were adhered onto negative electrostatic latent images, producing blackish purple images of little edge effect and high resolving power.

**COMPARATIVE EXAMPLES**

As part of experimental data on the various quantitative ratios between the dyestuff or dyestuff base and the fatty acid within the present invention, the results of using Nigrosine Base and various fatty acids are shown in Table 1.

The structural formula of Nigrosine Base is currently unestablished. Therefore its molecular weight was calculated from a presumed structural formula, and the weight ratios to realize the 1:1 mol ratio of Nigrosine Base and the fatty acids were determined as follows:

<table>
<thead>
<tr>
<th>Amount of fatty acid to 1 gram of Nigrosine Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>G.</td>
</tr>
<tr>
<td>Capric acid</td>
</tr>
<tr>
<td>Stearic acid</td>
</tr>
<tr>
<td>Oleic acid</td>
</tr>
<tr>
<td>Linoleic acid</td>
</tr>
</tbody>
</table>

In the runs wherein 2 molar times or more of the fatty acid of Nigrosine Base was used, the amount of the fatty acid was calculated as the multiple of the above-indicated amount of the specific acid employed. Each sample was prepared by taking the Nigrosine Base and fatty acid of the amounts specified into a beaker, and reacting them under stirring while heating in an oil bath. However, when the mol ratio of Nigrosine Base to the fatty acid was 1:1, 1:2, and 1:4, a minor amount of benzene was added to the system because the amount of the fatty acid was relatively too small to dissolve the Nigrosine Base. After the reaction under heating, the benzene was thoroughly removed by evaporation. Thus obtained salt-forming reaction products were each accurately weighed and dispersed in the carrier liquid at the predetermined concentration with the aid of ultrasonic waves. Also for examining the dispersibility of the reaction product in the carrier liquid, and changes in distinctness and fixing property of the images with time passage, the dispersions were allowed to stand in dark place at room temperature for a week.
| Table 1.—Properties of liquid developers containing salt-forming reaction products of nigrosine base with various fatty acids at varied mol ratios |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Dispersibility | Stability against time passage in image formation | Fixing property |
| Preparation time | After a week | Distinct image | Preparation time | After a week | Preparation time | After a week |
| Mol ratio of nigrosine base to fatty acid | Concentration of salt-forming reaction product in liquid developer (g/100 ml) | Electric charge of particles | Preparation time | After a week | Concentration of salt-forming reaction product in liquid developer (g/100 ml) | Electric charge of particles |
| 0.02 | 0.01 | 0.004 | 0.02 | 0.01 | 0.004 | 0.02 | 0.01 | 0.004 | 0.02 | 0.01 | 0.004 |
| Capric acid | | | | | | | | | | | | |
| 1:1 | Δ | — | — | X | — | — | + | Δ | — | — | X | — | — |
| 1:2 | o | o | o | Δ | X | X | x | o | o | o | Δ | X | X |
| 1:4 | o | o | o | Δ | Δ | X | X | o | o | o | Δ | Δ | X |
| 1:10 | o | o | o | Δ | Δ | Δ | X | o | o | o | Δ | Δ | Δ |
| 1:20 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:100 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:200 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:500 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:1000 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| Stearic acid | | | | | | | | | | | | |
| 1:1 | Δ | — | — | X | — | — | + | Δ | — | — | X | — | — |
| 1:2 | o | o | o | Δ | X | X | x | o | o | o | Δ | X | X |
| 1:4 | o | o | o | Δ | Δ | X | X | o | o | o | Δ | Δ | X |
| 1:10 | o | o | o | Δ | Δ | Δ | X | o | o | o | Δ | Δ | Δ |
| 1:20 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:50 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:100 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:200 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:500 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:1000 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| Oleic acid | | | | | | | | | | | | |
| 1:1 | Δ | — | — | X | — | — | + | Δ | — | — | X | — | — |
| 1:2 | o | o | o | Δ | X | X | x | o | o | o | Δ | X | X |
| 1:4 | o | o | o | Δ | Δ | X | X | o | o | o | Δ | Δ | X |
| 1:10 | o | o | o | Δ | Δ | Δ | Χ | o | o | o | Δ | Δ | Δ |
| 1:20 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:50 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:100 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:200 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:500 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| Linoleic acid | | | | | | | | | | | | |
| 1:1 | Δ | — | — | X | — | — | + | Δ | — | — | X | — | — |
| 1:2 | o | o | o | Δ | X | X | x | o | o | o | Δ | X | X |
| 1:4 | o | o | o | Δ | Δ | X | X | o | o | o | Δ | Δ | X |
| 1:10 | o | o | o | Δ | Δ | Δ | X | o | o | o | Δ | Δ | Δ |
| 1:20 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:50 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:100 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:200 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:500 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:1000 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| Stearic acid | | | | | | | | | | | | |
| 1:1 | Δ | — | — | X | — | — | + | Δ | — | — | X | — | — |
| 1:2 | o | o | o | Δ | X | X | x | o | o | o | Δ | X | X |
| 1:4 | o | o | o | Δ | Δ | X | X | o | o | o | Δ | Δ | X |
| 1:10 | o | o | o | Δ | Δ | Δ | X | o | o | o | Δ | Δ | Δ |
| 1:20 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:50 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:100 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:200 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:500 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |
| 1:1000 | o | o | o | Δ | Δ | Δ | Δ | o | o | o | Δ | Δ | Δ |

1 Isoparaffin hydrocarbon was used as carrier.
2 Temperature of liquid developer.
3 Whitekoh was used as carrier (Whitekoh: Tradename o the mixed solvent of aromatic hydrocarbon and aliphatic hydrocarbon, product of Kyodo Petroleum Co., Ltd.).
The norms of grading of properties indicated in the above table were as follows:

Dispersibility:
- Excellent dispersion showing no precipitate
- Good dispersion with a little precipitate
- Formation of considerable precipitate and supernatant liquid of low concentration
- Complete precipitation

Distinct images:
- Distinct contrast, sharp images and distinct print condition
- Sharp images but somewhat inferior contrast
- Very poor contrast or slight bleeding of the image
- Print condition showing image bleeding or very strong edge effect

Fixing property:
- No soiling of image takes place when the tester rubbed it strongly with finger.
- The image is not spoiled when the tester rubbed it with finger with normal force.
- The image is slightly spoiled when rubbed with finger with normal force.
- The image is spoiled when rubbed with finger.

The results indicated above demonstrate the following:
- Linoleic acid and oleic acid give liquid developers of good dispersibility under wide variety of conditions.
- Capric acid appears to give liquid developers of good dispersibility and fixing property only when used in larger quantities.
- Stearic acid gives poor results with isoparaffin type hydrocarbon as the carrier, because it is practically insoluble in the latter at room temperature, but gives satisfactory results with Whitesol which contains aromatic hydrocarbon.

EXAMPLE 2
To 50 g. of linoleic acid, 10 g. of Victoria Blue Base was added under stirring and completely dissolved. Thereafter the system was reacted for an hour at 120–150° C. The reaction product was allowed to stand to cool off of itself to 20–30° C., to provide a homogeneous, viscous salt-forming reaction product. One (1) g. of the product was added to 1 liter of Shellsol–71 (product of Shell Petroleum Co., an isoparaffin type solvent), forming a dispersion of extremely fine particles which were very stably and homogeneously suspended, with negligibly little precipitate. Two metal plates of electrodes were immersed in this liquid developer at face-to-face positions spaced by 1 cm., and direct current of 1,000 volts was applied for 60 seconds. Thereafter the state of adhesion of the particles to electrode surface was examined, confirming that the particles had 100% positive charge. The particles in the liquid developer were adhered onto negative electrostatic latent images, and formed blue image of good fixing property, little edge effect and high resolving power.

EXAMPLE 3
One hundred (100) g. of palmitic acid was heated to 70–80° C. to be liquefied, and into which 2 g. of Methyl Violet Base was gradually added with stirring. After the dyestuff base was completely dissolved, the solution was further heated to 100° C. and maintained at said temperature for an hour. The system was allowed to cool off of itself to 20–30° C., to provide a homogeneous, viscous salt-forming reaction product. Five (5) g. of this product was added to 1 liter of Isopar E (product of Esso Standard Petroleum Co., an isoparaffin type solvent) as the carrier liquid, to form a dispersion of extremely fine particles which were very stably and uniformly suspended in said carrier, producing substantially no precipitate. When the liquid developer was subjected to dispersing action of ultrasonic waves for further 1–2 minutes, the particle size was still reduced. The polarity of the particles was examined similarly to Example 2, to confirm that they were negatively charged. The liquid developer was repelled from negative electrostatic latent images, and formed violet, reversed images.

EXAMPLE 4
Ten (10) g. of stearic acid was heated to 80–100° C., and fused, and 1 g. of Indoline was added thereto gradually under stirring. The heating was continued for an hour, and thereafter 0.5 g. of the product still retaining the elevated temperature was added to 1 liter of Whitesol (product of Kyodo Petroleum Co.) acting as the insulative carrier liquid. Thus formed liquid developer may be further subjected to dispersing action of ultrasonic waves. With the developer, blackish purple images of high resolving power were obtained.

EXAMPLE 5
To 16 g. of lauric acid heated and fused at 50–60° C., 1 g. of Nigrosine Base was gradually added under stirring, and further heated for an hour. Separately, 50 cc. of New Sol Delux (product of Nippon Petroleum Co.) as an insulative carrier liquid was maintained at 60° C., and into which 1 g. of the above-obtained salt-forming reaction product was added and completely dissolved. The solution was then added to 950 cc. of same carrier liquid to provide a dispersion containing extremely fine particles without the aid of ultrasonic waves as mentioned in Example 4. This liquid developer was adhered onto negative electrostatic latent images, and formed blackish purple images of high resolving power.

EXAMPLE 6
To 10 g. of oleic acid, 1 g. of Bismarck Brown G Base was gradually added under stirring, to make a homogeneous mixture without containing large size blocks.

The mixture was heated to 90° C. and reacted for an hour, followed by natural cooling off to approximately 20° C. One (1) g. of this homogeneous, viscous salt-forming reaction product was added to 500 ml. of kerosine which was a petroleum type solvent, forming a liquid developer of excellent suspension quality in which the image-forming material was uniformly dispersed as fine particles. This developer formed substantially no precipitate after long period of storage, exhibiting very high stability. The polarity of charge of the particles in the developer was examined by inserting two metal plate electrodes in the developer at face-to-face positions spaced by 1 cm., and applying direct current of 1,000 volts (250 ma. current) for 60 seconds. Upon observing the adhering condition of the particles to the electrodes, it was confirmed that the particles were 100% negatively charged. Thus in actual printing, the developer served to form negative print from positive original, and positive print from negative original. The printed images exhibited good fixing property, little edge effect and high resolving power.

EXAMPLE 7
One (1) g. of Diacelliton Fast Brilliant Blue B (a disperse dye, product of Mitsubishi Kasei Kogyo K.K.) was added gradually to 30 g. of oleic acid under stirring, to form a homogeneous mixture, which was subsequently heated to 100–120° C. and stirred for 30 minutes to be reacted.

The reaction product was allowed to cool off of itself to approximately 20° C., and the unused charge by the method similar to that of Example 5, which precipitated was removed by filtration. One (1) g. of the reaction product was added to 1 liter of n-heptane and lightly stirred, to provide a liquid developer of excellent suspension quality and storage stability containing the finely dispersed particles. The polarity of the particles in the liquid developer as examined by the method similar to that of Example 5, was confirmed 100% positively. Therefore, the particles were adhered onto negative electrostatic latent images, forming blue images of
good fixing property, little edge effect and high resolving power.

EXAMPLE 8

To 60 g. of stearic acid heated to approximately 80° C., 3 g. of Magenta Base, a basic triphenylmethane dye-stuff base, was gradually added under stirring, to form a homogeneous and viscous salt-forming reaction product. Two (2) g. of this product was added to 50 cc. of mineral spirit, and the mixture was cooled to 100° C. to be dispersed as an extremely fine particle was obtained. Upon adding the resulting solution to 950 cc. of mineral spirit under stirring, a liquid developer of excellent suspension quality in which the salt-forming reaction product was dispersed as extremely fine particle was obtained. The polarity of the particles in the liquid developer was examined similarly to the foregoing example, to confirm that it was charged 100% negative. The liquid developer was adhered onto positive electrostatic latent images, and formed pink images of little edge effect and high resolving power. Also from negative electrostatic latent images, reversed images were obtained with this developer.

EXAMPLE 9

To 100 g. of linoleic acid, 10 g. of Methylene Blue Base, a quinonemine dye-stuff base, was added under stirring and completely dissolved, followed by heating to 120-150° C. for an hour to effect the reaction. The system was allowed to cool off of itself, to form a homogeneous, viscous salt-forming reaction product. One (1) g. of the product was added to 1 liter of dimethylsulfoxide and dispersed with ultrasonic waves. Thus a dispersion of fine particles of excellent suspension quality was obtained. The charge of the particles was examined similarly to the foregoing examples, to confirm that the particles were 100% positively electrified. This liquid developer was adhered onto negative electrostatic latent images, and formed blue images of good fixing property, little edge effect and high resolving power.

EXAMPLE 10

Ten (10) g. of Nigrosine Brown G Base were added little by little to 125 g. of oleic acid under stirring. Then the mixture was reacted for approximately an hour at 90-100° C. Thereafter, the system was allowed to cool off of itself to form a homogeneous, viscous salt-forming reaction product. Two (2) g. of this product was added to 1,000 ml. of Isopar H, an isoparaffin type hydrocarbon solvent, making a liquid developer in which the above product was dispersed as fine particles. The particles were 100% positively electrified, and adhered onto negative electrostatic latent images to form purely black images. Because the particles thus possessed 100% positive charge and were finely dispersed in the carried liquid, the developer exhibited high stability and resolving power.

What we claim is:

1. A liquid developer for electrophotography consisting of a dispersion of (A) a salt-forming reaction product of (a) at least one dyestuff or dye-stuff base containing amino groups selected from the groups consisting of basic azo dyes, basic diphenyl methane dyes, basic triphenyl methane dyes, acidine dyes, promine dyes, rhodamine dyes, quinoneimine dyes, azo type disperse dyes, anthraquinone dyes, and bases of these dyes, and (b) oleic acid in (B) a carrier consisting of (i) a high electric-resistant liquid selected from the groups consisting of liquid hydrocarbons, liquid halogenated hydrocarbons and silicon oils, and (ii) oleic acid dissolved in said high electric-resistant liquid, the total amount of said oleic acid (b) and oleic acid (ii) being from 10 to 400 mols per mol of said dyestuff or dyestuff base.

2. The liquid developer of claim 1 wherein said high electric resistance liquid has an electric resistance of not less than 10¹⁵Ω-cm.

3. The liquid developer of claim 2 wherein said high electric resistance liquid is a liquid hydrocarbon.

4. A liquid developer for electrophotography consisting of a dispersion of a salt-forming reaction product of (a) Nigrosine Base (C.I. 50415B), and (b) oleic acid in a carrier consisting of (i) a liquid hydrocarbon, and (ii) oleic acid dissolved in said liquid hydrocarbon, the total amount of said oleic acid (b) and oleic acid (ii) being from 10 to 400 mols per mol of said Nigrosine Base.

5. A liquid developer for electro-photography consisting of a dispersion of a salt-forming reaction product of (a) Victoria Blue Base (C.I. 4045B), and (b) oleic acid in a carrier consisting of (i) a liquid hydrocarbon, and (ii) oleic acid dissolved in said liquid hydrocarbon, the total amount of said oleic acid (b) and oleic acid (ii) being from 10 to 400 mols per mol of said Victoria Blue Base.

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U.S. Cl. X.R.

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